

Correlation between Mechanical Adhesion and Interfacial Properties of Starch/Biodegradable Polyester Blends

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ABSTRACT: Biopolymers are preferred ingredients for the manufacture of materials because they are based on abundantly available and renewable raw materials that have benign environmental problems associated with their production, fabrication, use, and disposal; however, the wide use of biopolymers in engineering applications has not been achieved, mainly because of the inferior quality of many biopolymer-based products. To overcome this limitation, studies have been initiated on blends of biopolymers and biodegradable synthetic polymers. We used the contact angle of probe liquids to measure the surface energy of polystyrene, the biodegradable polyesters polycaprolactone, poly(hydroxybutyrate-co-hydroxyvalerate), polylactic acid, polybutylene adipate terephthalate, and adipic poly(hydroxy ester ether), and normal starch. The surface energies were used to estimate the starch/polymer interfacial energy and work of adhesion. The calculated starch/polyester work of adhesion showed mixed correlation with published starch/polyester mechanical properties, indicating that factors other than interfacial properties might be dominant in determining the mechanical properties of some starch/polyester blends. © 2001 John Wiley & Sons, Inc. *J Polym Sci B: Polym Phys* 39: 920–930, 2001

Keywords: contact angle; surface tension; surface energy; interfacial energy; work of adhesion; peel strength; biodegradable polyesters; starch; polymers; blends

INTRODUCTION

Plant-based biopolymers such as starch, cellulose, and soy protein are preferred over synthetic polymers for the development of various materials for two major reasons:¹ (1) unlike petroleum-based synthetic polymers, they are based on abundantly available and renewable sources, and (2) because

of their biodegradability, their production, fabrication, use, and disposal present benign environmental problems. Despite these advantages, the development of materials from biopolymers is not widespread, mainly because of the inferior performance (e.g., poor water resistance) of products developed from biopolymers.²

One of the approaches being pursued to improve the performance of biobased materials in engineering applications is the blending of biopolymers with biodegradable synthetic polyesters.^{1,3} The goal of this approach is to develop biodegradable materials with acceptable material properties from blends comprising mostly biopolymers. Synthetic polyesters that have been used in such studies involving starch blends include polycaprolactone (PCL),⁴ poly(hydroxybutyrate-co-

Names are necessary to report factually on available data; however, the U.S. Department of Agriculture (USDA) neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

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Table I. Polymers Used in this Work

Polymer (Designation)	Source	T_g (°C)	Molding Temperature (°C)
Polycaprolactone (PCL 787)	Union Carbide	-60	120
Polybutylene adipate terephthalate (Copolyester 14766)	Eastman	-30	138
Poly(hydroxybutyrate-co-hydroxyvalerate), 12.3% V (PHB12HV)	Zeneca	-1	170
Adipic poly(hydroxyester ether) (PHEE)	Dow	42	150
DL-Polylactic acid (PLA)	Cargill	57-60	172
Polystyrene (PS)	GE	100	175

hydroxyvalerate) (PHBHV),⁵ and polylactic acid (PLA).⁶

Most previous studies of starch/polyester blends have focused on mechanical, thermal, and/or rheological properties.¹ There have also been studies aimed at characterizing the surface properties of biodegradable polyesters⁷⁻¹⁴ and starch,⁷⁻¹⁷ but there has not been any work aimed at characterizing starch/polyester interfacial properties and correlating them to blend mechanical properties. In this article, we present the results of our investigation into the interfacial properties of blends of starch with a number of biodegradable polyesters. We also compared our interfacial results with published peel-strength data of starch/polyester blends.

Polymer compatibility is an important factor in the development of polymer blends. Compatibility is critical in governing the morphology of the blend and, therefore, the final-state physical and mechanical properties of the system. One of the major governing factors that control the compatibility in polymer blends is interfacial tension.¹⁸ The interfacial energy of polymer blends can be measured directly or calculated from the surface energy and other properties of blend components.^{19,20} The surface energies of polymers used in interfacial-energy calculations can be obtained by direct measurement or derived from contact-angle measurements of probe liquids on the polymers.^{19,20}

Current methods for the direct measurement of the surface energies of polymers require that the polymer melt at reasonable temperatures into low-viscosity liquids and also remain stable during the time required to attain equilibrium and complete the measurement. We elected to employ an indirect method for estimating the surface energy of the polyesters used in this work, mainly because we do not know if the materials studied

herein meet the criteria stated previously. Also, current methods for the measurement of interfacial energies cannot be used on starch blends, mainly because of difficulties of maintaining the moisture content of starch at the measurement temperature. The melting point of starch is highly dependent on the concentration of water or other plasticizers.¹

In this work, the contact angle of water, methylene iodide, and dimethyl sulfoxide (DMSO) probe liquids were used to measure the surface energy of PCL, PHBHV, PLA, adipic poly(hydroxy ester ether) (PHEE),²¹ polybutylene adipate terephthalate (Copolyester 14766),²² and polystyrene (PS) with the procedure of van Oss, Chaudhury, and Good (VCG).²³⁻²⁵ The same procedure was also used to obtain the surface energy of starch from the reported contact angle of water, methylene iodide, and glycerol.¹⁵ The surface energies were then used to calculate starch/polymer interfacial energy and work of adhesion.

EXPERIMENTAL

Materials

PS, PCL 787, PHBHV with 12.3% valerate content (PHB12HV), PLA, Copolyester 14766, and PHEE were commercially obtained and used as supplied. Pertinent details about these polymers are summarized in Table I.

The probe liquids DMSO (>99.9%) and diiodomethane (MeI₂; >97%) were obtained from Alfa Aesar (Ward Hill, MA) and used without further purification. Deionized water further purified with a Milli-Q system (18.0 mΩ/cm) was used exclusively in this work.

Polymer Sample Preparation

Polymer films (5 in. × 5 in. × 0.0625 in.) were compression-molded on a Carver laboratory press

(Wabash, IN) equipped with a water-cooling system. The films were then cut into 15 mm \times 30 mm specimens on a precision CO₂ laser cutting machine (Kern Electronics & Lasers, Inc., Wadena, MN), stored in a refrigerator at 3 °C, and then allowed to warm up to room temperature before use in contact-angle measurements.

Compression-Molding Apparatus

The molding apparatus includes a stainless steel mold plate sandwiched between top and bottom stainless steel cover plates. The cover plates were lined with Bytac® AF-21 nonstick aluminum foil (Daigger Co., Lincolnshire, IL) to allow for easy release of the polymer film from the mold. With the exception of the molding temperatures, which are given in Table I, the same molding procedure was used on all the polymers. Care was taken to prevent contamination of the polymer film surface during compression molding and subsequent manipulations.

Polymer Compression-Molding Procedure

The mold setup, without the polymer pellets, was placed in the press and heated to the molding temperature, with the platens contacting both the top and bottom cover plates. The temperature was maintained for 30 min, after which the setup was removed, the resin was introduced, and the setup was returned to the press quickly to minimize excessive cooling of the mold setup. The temperature was maintained for another 10 min, after which the pressure was gradually increased to 30–35 kpsi over 10 min. The pressure and temperature were maintained for another 10 min, after which the platens were cooled while the pressure was maintained. The pressure was released as soon as the platen temperatures cooled below the glass-transition temperature of the polymer.

Contact-Angle Measurement

Contact-Angle Measurement Apparatus

The contact angle of sessile drops of the probe liquids on the polymers was measured with an FTA 200 automated goniometer (First Ten Angstroms, Portsmouth, VA). A schematic of the instrument is shown in Figure 1. The main features of this instrument relevant to this work are an automated pump that can be fitted with various sizes of syringes and needles to allow for the con-

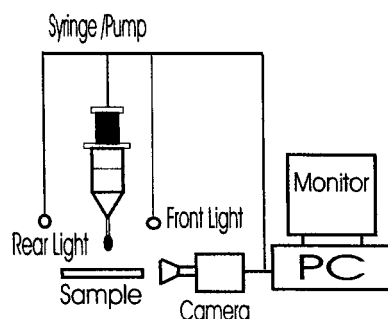


Figure 1. Schematic of an automated goniometer.

trol of drop application, an automated image-viewing and -capturing system with various image-capture triggering options, and software for measuring the contact angle via an automated drop-shape analysis of the drop image. In this work, all measurements were conducted with 10-mL disposable syringes (Becton Dickinson & Co., Franklin Lakes, NJ) equipped with 22-gauge blunt disposable needles (KDS21-1P, Kahnetics Dispensing Systems, Bloomington, CA). A manual trigger was used to initiate the capture of a total of 20 images of the drop at a rate of 0.033 s/image. The contact angle from each image and the average contact angle for the drop were obtained after each measurement.

Contact-Angle Measurement Procedure

In a typical procedure, the needle position was first adjusted to minimize the fall distance of the drop onto the polymer surface. The pump was started, and the liquid was automatically pumped at 0.1 μ L/s. The capture was triggered as soon as the drop reached the surface. Each image was automatically analyzed, and the contact angle as a function of time and the average contact angle of the drop was displayed. All measurements were conducted at room temperature (22 ± 1 °C).

RESULTS AND DISCUSSION

Wettability Methods of Solid Surface-Energy Estimation

The total surface energy of a solid is the sum of the dispersive and polar surface-energy components,^{19,20} as shown in eq 1. It can be measured from the contact angle (θ) of the probe liquids whose total, dispersive, and polar surface tensions have been independently determined:

$$\gamma_S^{\text{TOT}} = \gamma_S^D + \gamma_S^P \quad (1)$$

The basis of the wettability method is the Young–Dupre equation,^{19,20} which relates the surface tension and contact angle of a liquid to the solid/liquid work of adhesion (W_{SL}). The latter is a function of the liquid surface tension and the solid surface energy (eq 2), and this relationship is used to extract the solid surface energy from the contact angle and independently determined surface-energy parameters of the probe liquid(s):

$$\gamma_L^{\text{TOT}}[1 + \cos(\theta)] = W_{\text{SL}} = f(\gamma_S^{\text{TOT}}, \gamma_L^{\text{TOT}}) \quad (2)$$

Depending on the method used to relate W_{SL} to the energy parameters, the surface energy of a solid can be determined from the contact angle of one, two, or three probe liquids. A brief description of each of these methods is given next.

Single-Probe-Liquid Method

This method is used for solids that are totally nonpolar [e.g., polytetrafluoroethylene (PTFE)] or when the polar components are small and one chooses to ignore them. The total surface energy of the solid is determined from the contact angle of a single nonpolar probe liquid such as MeI₂ ($\gamma_L^D = \gamma_L^{\text{TOT}}$) with eq 3:^{19,20,26}

$$\gamma_S^{\text{TOT}} = \gamma_S^D = \left(\frac{1}{4}\right)[\gamma_L(1 + \cos \theta)^2] \quad (3)$$

Two Probe-Liquid Method

This method is used for solids with a significant polar surface-energy component. It requires the use of two probe liquids, one nonpolar and one polar. There are two different approaches in the two-probe-liquid method; they are designated the *geometric mean* (GM) and *harmonic mean* (HM) approaches. In both cases, the dispersive component of the solid surface energy (γ_S^D) is first determined from the contact angle of the nonpolar liquid with eq 3 in the GM approach and with eq 4 in the HM approach:

$$\gamma_S^D = [\gamma_L^{\text{TOT}}(1 + \cos \theta)]/[3 - \cos(\theta)] \quad (4)$$

The polar component of the solid surface energy (γ_S^P) is then calculated using the calculated γ_S^D values, the contact-angle and surface-tension components (γ_L^D , γ_L^P , and γ_L^{TOT}) of the polar probe liquid, and eq 5 in the GM approach:

$$\gamma_S^P = [(A - B)^2]/[4\gamma_L^P] \quad (5)$$

or eq 6 in the HM approach:

$$\gamma_S^P = [(\gamma_L^P)(A - C)]/[4\gamma_L^P - (A - C)] \quad (6)$$

where $A = \gamma_L^{\text{TOT}} [1 + \cos(\theta)]$, $B = 2 [\gamma_S^D \gamma_L^D]^{0.5}$, and $C = [4\gamma_S^D \gamma_L^D]/[\gamma_S^D + \gamma_L^D]$

Three-Probe-Liquid Method

Determination of the surface energy of solids by the VCG method requires the use of three probe liquids.^{23–25} In this approach, the dispersive energy is called the *Lifshitz–van der Waals energy* ($\gamma_S^{\text{LW}} = \gamma_S^D$). However, the polar surface energy, which is called the *acid/base surface energy* ($\gamma_S^{\text{AB}} = \gamma_S^P$), is calculated from the acid/base property, that is, the electron acceptor/donor or hydrogen-bond donor/acceptor properties (γ_S^+ , γ_S^-), of the solid as follows:

$$\gamma_S^P = \gamma_S^{\text{AB}} = 2[\gamma_S^+ \gamma_S^-]^{0.5} \quad (7)$$

As a result, the total surface energy is expressed in terms of three surface-energy parameters (γ_S^{LW} , γ_S^+ , γ_S^-):

$$\gamma_S^{\text{TOT}} = \gamma_S^{\text{LW}} + \gamma_S^{\text{AB}} = \gamma_S^{\text{LW}} + 2[\gamma_S^+ \gamma_S^-]^{0.5} \quad (8)$$

Thus, three probe liquids will be required to determine the total surface energy of polar solids with the VCG method. To do this, first γ_S^{LW} is determined from the contact angle of a nonpolar probe liquid (for which $\gamma_L^{\text{AB}} = 0$) with eq 3. Then, γ_S^+ and γ_S^- are determined by the solution of the simultaneous equation obtained by the contact angle and independently determined surface-energy parameters (γ_L^{TOT} , γ_L^{LW} , γ_L^+ , γ_L^-) of the two polar probe liquids being inputted into eq 9:

$$[\gamma_S^+ \gamma_L^-]^{0.5} + [\gamma_S^- \gamma_L^+]^{0.5} = 0.5[A - B] \quad (9)$$

where $A = \gamma_L^{\text{TOT}} [1 + \cos(\theta)]$ and $B = 2[\gamma_S^{\text{LW}} \gamma_L^{\text{LW}}]^{0.5}$.

Contact Angles of Probe Liquids on Candidate Polymers

The contact angles of sessile drops of water, CH₂I₂, and DMSO probe liquids on specimens of compression-molded PHEE, PS, PLA, PCL, PHB12HV, and copolyester 14766 were measured

Table II. Average Contact Angles (Standard Deviation) of the Probe Liquids on the Polymers at 22 ± 1 °C (degrees)

Polymer	Water	Glycerol	CH ₂ I ₂	DMSO	Reference
PCL 787	70.7 (4.3)	—	27.7 (4.3)	32.5 (3.7)	This work
Copolyester 14766	62.2 (2.7)	—	30.8 (0.9)	36.9 (2.0)	This work
PHB12HV	61.4 (1.2)	—	36.5 (2.5)	43.2 (3.2)	This work
PHEE	86.4 (6.5)	—	51.0 (4.4)	58.9 (5.8)	This work
PLA	67.7 (4.0)	—	40.1 (3.3)	30.9 (4.0)	This work
PS	89.0 (3.9)	—	41.3 (4.5)	35.0 (3.6)	This work
PS	91	—	—	—	20
Normal starch	84.9 (5.9)	74.0 (6.6)	35.6 (4.6)	—	15

on an automated goniometer. The instrument allows for the automated placement and imaging of drops and the automatic calculation of the contact angle from each image with drop-shape analysis software.

For each probe-liquid/polymer combination, a total of 12–60 drops on three to four polymer specimens were imaged. The standard deviations of individual measurements were less than 1°, with most measurements showing standard deviations below 0.5°. The average contact angle and standard deviation for each polymer/probe-liquid combination are summarized in Table II. Also summarized in Table II are literature contact-angle values of water, CH₂I₂, and glycerol on normal starch.¹⁵ As shown in Table II, the contact angle of water on PS obtained in this work was $89.0 \pm 3.9^\circ$, which is equivalent to the reported²⁰ value of 91° .

A literature search produced several reports of water contact angles on PLA,^{2,7,27–29} PCL,^{9,11,30–32} and PHBH^{12,13,33,34} of various hydroxyvalerate (HV) contents; one report each for the CH₂I₂ contact angle on PLA⁷ and PCL¹¹; and no contact-angle reports for PHEE and Copolyester 14766. The reported contact-angle values along with the quoted standard deviations are summarized and compared with the results from this work in Table III.

The summary in Table III shows that the contact angles of CH₂I₂ on PLA and PCL from this work were similar to the literature values.^{7,11} However, the contact angles of water on these two polyesters were highly dependent on the methods used for sample preparation and measurement of the contact angles. Thus, higher contact angles were reported on melt or solution-cast samples than on injection or compression-molded samples. Also, higher values were reported with the Wilhelmy fiber and Wilhelmy plate methods than

with the sessile drop method of contact-angle measurement.

Table III also shows that all previous water contact-angle data^{12,13,33,34} on PHBH_nHV are higher than our values and were obtained on solution-cast samples, which is consistent with the trend described previously for PLA and PCL. The data in Table III also show that increasing the composition of HV in PHBH_nHV results in increasing the contact angle of water, an indication of increased hydrophobicity of the surface due to the increased concentration of HV segments on the surface.

In general, the data in Table III show that the contact angles from this work are similar to literature values obtained on noncast samples with the sessile drop method.

Estimation of the Surface Energy of Candidate Polymers

The contact angles of water, CH₂I₂, and DMSO measured in this study and shown in Table II and their surface-tension parameters (shown in Table IV) were used to estimate the various surface-energy parameters of PHEE, PS, PLA, PCL, PHB12HV, and copolyester 14766 polymers with the three-liquid-probe (VCG) procedure described previously. With this procedure, γ_S^{LW} , γ_S^{AB} , γ_S^+ , γ_S^- , and γ_S^{TOT} were calculated with eqs 3, 7, 8, and 9. The same procedure was used to calculate the corresponding values for normal starch with the reported¹⁵ contact-angle values of water, CH₂I₂, and glycerol, which are also shown in Table II.

The calculated values of the various surface-energy parameters are summarized in Table V. Also shown in Table V are the standard deviations associated with γ_S^{LW} of the polymers, which was estimated from the contact angle and γ_S^{LW} of CH₂I₂, for which the standard deviation values

Table III. Effect of the Sample Preparation and Contact-Angle Measurement Methods on Room-Temperature $\theta_{\text{H}_2\text{O}}$ and $\theta_{\text{CH}_2\text{I}_2}$ (degrees)

Sample Preparation Method	Contact Angle Method ^a	PLA		PCL		PHBnHV ^b		Reference
		$\theta_{\text{H}_2\text{O}}$	$\theta_{\text{CH}_2\text{I}_2}$	$\theta_{\text{H}_2\text{O}}$	$\theta_{\text{CH}_2\text{I}_2}$	n^b	$\theta_{\text{H}_2\text{O}}$	
Blown film	NS	73 ^c						2
Injection mold	NS			71 ^c	25 ^c			11
Compression mold	SD	67.7 ± 4.0	40.1 ± 3.3	70.7 ± 4.3	27.7 ± 4.3	12.3	61.4 ± 1.2	This work
Cast LB film	SD	41–73 ± 1.0	41–47 ± 1.0					7
Melt- or solution-cast	SD	76 ^c						27
Melt-cast	SD			75 ± 3				30
Melt-cast	SD			89 ± 2				9
Solution-cast	SD			69 ^c				31
Solution-cast	SD			80 ^c				31
Solution-cast	SD					0	64.1 ± 0.2	33
Solution-cast	SD					7	90.0 ± 3.8	34
Solution-cast	SD					9	71 ± 1.0	12, 13
Solution-cast	SD					9	69.5 ± 0.2	33
Solution-cast	SD					14	75.7 ± 1.9	34
Solution-cast	SD					22	75.0 ± 0.2	33
Solution-cast	SD					22	73.9 ± 3.0	34
Commercial film ^d	SD			91 ± 1				32
Solution-cast	WP	80–95 ^c						28
Melt-spun	WF	84 ^c						29
Melt-spun	WF	94 ^c						29

^a Contact-angle measurement methods: NS, not specified; SD, sessile drop; WP, Wilhelmy plate; and WF, Wilhelmy fiber.

^b Where n is the HV percentage in PHBnHV (e.g., PHB9HV contains 9% HV, whereas PHB0HV contains no HV).

^c Standard deviation values not reported.

^d Commercial film; the sample preparation method is not specified.

are known (see Table IV). The standard deviations for γ_{S}^+ and γ_{S}^- values of the polymers could not be determined because the corresponding values for the probe liquids are not available (see Table IV). γ_{S}^+ and γ_{S}^- for water were arbitrarily assigned at 25.5 dyn/cm, which was then used to estimate the γ_{S}^+ and γ_{S}^- values for other probe liquids.²⁵

As shown in Table V, our results for $\gamma_{\text{S}}^{\text{TOT}}$ of PS was 40.0 dyn/cm, which is similar to the literature value of 40.7 dyn/cm.²⁰ A literature search produced estimates of surface-energy parameters for PLA^{7,8,14} and PCL^{9–11,14} with the VCG, GM, and HM methods; for PHBHV^{12–14} with the HM and GM methods; and for starch^{14–17} with the HM and nonwettability methods. There were no re-

Table IV. Surface-Tension Parameters (Standard Deviation) of the Probe Liquids at 20 °C (dyn/cm)^a

	γ^{TOT}	γ^{LW}	γ^{AB}	γ^+	γ^-
Water	72.28 (0.2 ^b)	21.8 (0.7 ^c)	51.0	25.5	25.5
CH ₂ I ₂	50.8 (0.2 ^b)	50.8 (0.2 ^b)	0	0	0
DMSO	44 (0.2 ^b)	36	8	0.5	32
Glycerol	64 (0.2 ^d)	34	30	3.92 (0.7 ^e)	57.4

^a Values of the surface-tension parameter are from Table XIII-10 of ref. 25. Standard deviation values were obtained from various sources.

^b Jasper, J. J. J Phys Chem Ref Data 1972, 1, 841–1009.

^c Fowkes, F. M. J Phys Chem 1963, 67, 2538–2541.

^d Eagland, D.; Midgley, B.; Hughes, I. S. J Colloid Interface Sci 1990; 136:327–337.

^e van Oss, C. J.; Good, R. J.; Busscher, H. J. J Dispersion Sci Technol 1990; 11:75–81.

Table V. Surface-Energy Parameters of the Polymers and Starch Calculated from Room-Temperature (22 ± 1 °C) Contact Angles of the Probe Liquids with the VCG Procedure (dyn/cm)

Polymer	γ^{TOT}	γ^{LW}	γ^{AB}	γ^+	γ^-	Reference
PHEE	34.7	33.7 ± 2.5	1.0	0.068	3.9	This work
PS	40.0	39.0 ± 2.3	1.0	0.21	1.1	This work
PS	40.7	—	—	—	—	20
PHB12HV	42.2	41.3 ± 1.2	0.9	0.0088	20.7	This work
PLA	43.5	39.6 ± 1.7	3.9	0.31	12.2	This work
Copolyester 14766	44.2	43.9 ± 0.4	0.3	0.00082	18.9	This work
PCL 787	45.5	45.2 ± 1.7	0.3	0.0018	10.6	This work
Normal starch	43.0	41.8 ± 2.2	1.2	0.17	2.0	This work

ported estimates for the surface-energy parameters of PHEE and Copolyester 14766. The surface-energy parameters from the literature and this work, along with the corresponding standard deviations if reported, are compared in Table VI. In general, our $\gamma_{\text{S}}^{\text{TOT}}$ values for the polyesters were similar to those reported on molded samples.

An examination of Table VI shows that our $\gamma_{\text{S}}^{\text{TOT}}$ values for PLA are similar to literature data except for some cast Langmuir–Blodgett (LB) films, whose surface energy was dependent on the properties of the spreading solvent and the surface property of the substrate used for casting the LB film.⁷ $\gamma_{\text{S}}^{\text{TOT}}$ values for PCL from this work were similar to literature values on molded^{10,11} samples but higher than those on cast^{9,14} samples. Our $\gamma_{\text{S}}^{\text{TOT}}$ values for PHB12HV were similar to a previous estimate¹⁴ on the same polymer. However, reported $\gamma_{\text{S}}^{\text{TOT}}$ values of PHB9HV^{12,13} are higher and could be an indication of a more polar surface than PHB12HV.

Values of $\gamma_{\text{S}}^{\text{TOT}}$ of starch from this work were close to the higher end of the reported range of $\gamma_{\text{S}}^{\text{TOT}}$ values for normal, high amylose and waxy starch obtained with wettability methods.¹⁵ However, our $\gamma_{\text{S}}^{\text{TOT}}$ values were much lower than those reported with group-contribution¹⁴ or other non-wettability methods.¹⁶

Tables V and VI show that $\gamma_{\text{S}}^{\text{TOT}}$ values obtained in this work were within 10% of the values reported in the literature with wettability methods on comparable samples of PS, PLA, PCL, PHB12HV, and normal starch. Our $\gamma_{\text{S}}^{\text{TOT}}$ values increased in the order PHEE < PS < PHB12HV < PLA < Copolyester 14766 < PCL, which is similar to the trends in the available $\gamma_{\text{S}}^{\text{TOT}}$ literature data on comparable samples, that is, PS < PHB12HV < PLA < PCL (Tables V and VI).

Effect of the Sample Preparation Methods on the Contact Angle and Surface Energy of the Polymers

The dramatic effects of the sample preparation technique on the contact angle and surface energy of polymers (shown in Tables III and VI) are well known and documented.^{35–39} The surface energy of polymers, melt-cast under nitrogen or air on various substrates, showed large variations depending on the properties of the substrate.^{36,37} Thus, polyethylene cast under nitrogen on various substrates showed the same surface energy on the nitrogen side, regardless of the substrate, which was equal to the surface energy on the substrate side for PTFE and polyethylene terephthalate substrates (36.2 dyn/cm). However, the surface energies were higher on the substrate side for glass, chromium, mercury, and gold substrates: 54.9, 56.1, 64.8, and 69.9 dyn/cm, respectively.³⁶ Similar results were reported by Tamai and Tanaka³⁷ on a copolymer plastic film. Solution-casting and melt-casting processes are generally slower than compression-molding and injection-molding processes and allow polymer molecules to rearrange in response to the requirements imposed by the substrate surface. This explains the differences in the reported contact angles and surface energies of the polyesters used in this study.

Estimation of the Starch/Polymer Interfacial Energy and Work of Adhesion

The surface-energy parameters of PHEE, PS, PLA, PCL, PHB12HV, Copolyester 14766, and normal starch determined in this work and shown in Table V were used to estimate the starch/polymer interfacial energy ($\gamma_{\text{SP}}^{\text{TOT}}$) with the VCG method²⁴ (eq 10). The resulting interfacial ener-

Table VI. Comparison of the Room-Temperature Surface-Energy Parameters (dyn/cm)^a

Polymer	Sample Preparation	Contact-Angle Method ^b	Surface-Energy Estimation Method ^c	γ^{TOT}	$\gamma^{\text{LW}} (\gamma^D)$	$\gamma^{\text{AB}} (\gamma^P)$	γ^+	γ^-	Reference
PLA	Compression-molded	SD	VCG	43.5	39.6 ± 1.7	3.9	0.31	12.2	This work
PLA	Cast LB film	SD	VCG	40.24	36.0	4.24	0.1	44.9	7
PLA	Cast LB film	SD	VCG	36.6	36.6	0	0	20.5	7
PLA	Cast LB film	SD	VCG	35.9	35.9	0	0	15.3	7
PLA	Melt-extruded	SD	HM/GM	43.5					8
PLA	Solution-cast	WP	HM	43.9					14
PCL	Compression-molded	SD	VCG	45.5	45.2 ± 1.7	0.3	0.0018	10.6	This work
PCL	Melt-cast	SD	VCG	26.5	24.4	2.1	0.22	5.24	9
PCL	Vacuum-molded	SD	HM	45.5, 44.0	35.2, 37.0	10.3, 7.0			10
PCL	Injection-molded	NS	HM/GM	48.3	41.9	6.4			11
PCL	Solution-cast	WP	HM	39.6					14
PHB12HV	Compression-molded	SD	VCG	42.2	41.3 ± 1.2	0.9	0.0088	20.7	This work
PHB12HV	Solution-cast	WP	HM	41.3					14
PHB9HV	Solution-cast	SD	GM	48.5 ± 1.0	42.2 ± 1.0	6.3 ± 1.0			12, 13
N starch	Melt-extruded	WP	VCG	43.0	41.8 ± 2.2	1.2			This work
N starch	Melt-extruded	WP	HM	35.7–40.1	27.5–37.0	1.4–10.0	0.17	2.0	15
HA starch	Melt-extruded	WP	HM	37.9–41.2	33.5–38.6	0.2–7.7			15
W starch	Melt-extruded	WP	HM	36.4–38.9	28.9–35.0	1.4–10.0			15
N starch	Aqueous solution	—	DN	58.7 ± 0.2	27.4				16
N starch	—	—	IGC						17
N starch	—	—	GC	53.7					14

^a Standard deviation values are reported very rarely and are shown here when available.^b Contact-angle methods: SD, sessile drop; WP, Wilhelmy plate; and NS, not specified.^c Surface-energy estimation methods: DN, du Nouy ring tensiometry; GC, group contribution; GM, geometric mean; IGC, inverse gas chromatography; HM, harmonic mean; and VCG, van Oss-Chaudhury-Good.

Table VII. Calculated Starch/Polymer Interfacial Energy and Work of Adhesion at 22 ± 1 °C (dyn/cm)

Polymer	Starch/Polymer Interfacial Energy	Starch/Polymer Work of Adhesion
Copolyester 14766	-2.2	89.3
PHB12HV	-2.0	87.1
PCL 787	-1.3	89.7
PS	0.022	82.8
PHEE	0.25	77.4
PLA	0.61	85.8

gies were then used to estimate the starch/polymer work of adhesion with eq 11:

$$\gamma_{SP}^{TOT} = [\sqrt{\gamma_S^{LW}} - \sqrt{\gamma_P^{LW}}]^2 + 2*[\sqrt{\gamma_S^+ \gamma_S^-} + \sqrt{\gamma_P^+ \gamma_P^-} - \sqrt{\gamma_S^+ \gamma_P^-} - \sqrt{\gamma_S^- \gamma_P^+}] \quad (10)$$

$$W_{SP} = \gamma_S^{TOT} + \gamma_P^{TOT} - \gamma_{SP}^{TOT} \quad (11)$$

The calculated values are summarized in Table VII. As mentioned previously, the standard deviations associated with the calculated γ_{SP}^{TOT} and W_{SP} values could not be determined because of the lack of standard deviation data on the γ^+ and γ^- values of the probe liquids.

The results in Table VII indicate that the starch/polymer interfacial energy increased in the order starch/copolyester 14766 < starch/PHB12HV < starch/PCL < starch/PS < starch/PHEE < starch/PLA, whereas the starch/polymer work of adhesion decreased in the order starch/PCL > starch/Copolyester 14766 > starch/PHB12HV > starch/PLA > starch/PS > starch/PHEE.

Adhesion in Starch/Polyester Composites

There are two reports dealing with a systematic study of adhesion between starch and biodegradable polyesters.^{14,40} In both studies, adhesion was evaluated with 90° peel tests at a peel rate of 50.8 mm/min. However, the two studies differ in the method used for preparing the peel-test samples. In the first study,¹⁴ peel-test samples were prepared by the polyester being applied onto starch foams with a brush from an appropriate solvent. In the second study,⁴⁰ peel-test samples were prepared by a three-layer polyester–starch–polyester coextrusion. The peel-strength values from these

two studies are compared in Table VIII. As shown in Table VIII, the peel-strength values from the first study were about five times bigger than those from the second study. This was attributed to improved starch/polyester adhesion due to the roughness of the starch foam used in the first study. However, despite the differences in the absolute values, the trends in peel-strength data of polyesters used in both studies were similar. Thus, a trend in peel-strength of PLA > PCL was observed in both studies.

The peel-strength data from the two systematic studies discussed above need to be normalized before they can be used in a quantitative correlation with the work of adhesion from this work. At this time, there are no obvious methods for carrying out such normalizations, and a qualitative comparison of trends in the measured starch/polyester peel strength versus the calculated work of adhesion is given next.

Table IX compares the trends in the work of adhesion with trends of reported peel-strength data^{14,40} of starch/PLA, starch/PCL, starch/PHB12HV, and starch/Copolyester 14766 composites. As shown in Table IX, the trends in the reported peel-strength data show mixed correlation with the trend in the work of adhesion data obtained from this work. Thus, correlation between peel strength and work of adhesion was observed for starch/PCL, starch/PHB12HV, and starch/Copolyester 14766 composites but not for starch/PLA composites. This mixed correlation is particularly serious because PLA comes out as the least compatible with starch from this work but shows the highest reported peel strength.

Table VIII. Reported Peel Strengths of Starch/Polyester Composites (N/mm)^a

Polyester	Polyester Applied onto Starch Foams from a Solution with a Brush	Three-Layer Coextrusion of Polyester/Starch/Polyester
PHBV	0.039 ^b	
PCL 787	0.103 ^b	0.02 ± 0.01
Copolyester 14766		0.01 ± 0.01
PLA	0.230 ^b	0.05 ^c
Source	Ref. 14	Ref. 40

^a (Instron) 90° peel test at a peel rate of 50.8 mm/min.

^b Standard deviation not reported.

^c Polymer films were difficult to peel off without the film breaking.

Table IX. Trends in the Reported Room-Temperature Interfacial and Mechanical Properties of Starch/Polyester Blends

Property	Trend	Reference
γ_{ij}	Copolyester 14766 < PHB12HV < PCL 787 < PS < PHEE < PLA	This work
W_{ij}	PCL 787 > Copolyester 14766 > PHB12HV > PLA > PS > PHEE	This work
Peel strength	PLA > PCL 787 > PHB12HV	14
Peel strength	PLA > PCL 787 > Copolyester 14766	40

Adhesive strengths obtained with peel tests and similar techniques are functions of various factors,⁴¹ including interfacial energy, interfacial reaction, and diffusion. Other factors that have a significant influence on the observed bond strengths include the viscoelastic and mechanical properties of the two components, which constitute the interface.^{18,19,35} Localized yielding along the interfacial region can contribute to higher values for the effective bond strength of the material than interfacial adhesion values alone would indicate. Such localized yielding will, in turn, be affected by the relative temperature dependence of the mechanical properties of the two component materials. Materials with lower glass-transition temperatures will, in general, exhibit more yielding behavior as the fracture surface passes through the interface because of localized heating effects. In addition, the failure of a bonded material may actually occur within one of the materials and not specifically in the interface region. Such failures are called *cohesive failures*, and, in many cases, it is difficult to determine the extent of cohesive failure relative to the extent of failure in the interfacial region. The presence of cohesive failure during a measurement, if not properly taken into account, can raise or lower the quoted interfacial bond strength. In addition to these difficulties, the type of measurement method employed can also lead to variations in the quoted bond strengths. It is clear from this study that mechanisms other than interfacial tension might be the dominant factors in starch/PLA blends. These factors have to be investigated to understand the mixed correlation between the work of adhesion and peel strength of the starch/polyester composites shown in Table IX. Work at understanding interactions of starch/polyester blends, including those of starch/PLA blends, is in progress.

SUMMARY AND CONCLUSION

The surface energies of PS and the biodegradable polyesters PCL, PHB12HV, PLA, Copolyester

14766, and PHEE were determined from the contact angles of water, methylene iodide, and DMSO probe liquids with the VCG procedure.^{23–25} The surface energy of starch was also determined with the same procedure and reported contact angles of water, methylene iodide, and glycerol on normal starch.¹⁵ The results were then used to estimate the starch/polymer interfacial energy and work of adhesion. The starch/polymer interfacial energy increased in the order starch/Copolyester 14766 < starch/PHB12HV < starch/PCL < starch/PS < starch/PHEE < starch/PLA. The starch/polymer work of adhesion decreased in the order starch/PCL > starch/Copolyester 14766 > starch/PHB12HV > starch/PLA > starch/PS > starch/PHEE. A comparison of the trends in the work of adhesion from this work with reported peel strengths of starch/polyester blends showed mixed correlations. Thus, a correlation in trends of the work of adhesion and peel strength was observed for starch/PCL, starch/PHB12HV, and starch/Copolyester 14766 composites but not for starch/PLA composites. It is proposed that mechanisms other than interfacial tension might be the dominant factors in starch/PLA blends.

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